CM 3539

PATENT SPECIFICATION

(11) **1213 697**

1213697

NO DRAWINGS

(21) Application No. 19788/68 (22) Filed 26 April 1968
(31) Convention Application No. T 33768 IVa/30h
(32) Filed 29 April 1967 in
(33) Germany (DT)
(45) Complete Specification published 25 Nov. 1970
(51) International Classification D 06 p 1/32
(52) Index at acceptance D1B 2A3

(54) IMPROVEMENTS IN DYEING HAIR

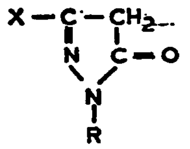
(71) We, THERACHEMIE CHEMISCH THERAPEUTISCHE GESELLSCHAFT MBH., a German Company, of 86—88 Schadowstrasse, 4000 Duesseldorf, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a composition and process for dyeing human hair based on oxidation colours.

It is not novel to dye human hair with oxidation dyestuffs which are developed with atmospheric oxygen or chemical oxidation agents. In particular it is known, to use for this purpose, substances containing p - amino - dimethylaniline combined with 1 - phenyl - 3-methylpyrazolone.

It has now been discovered that the colour intensity and other properties of the dyes can be improved by using the compositions comprising a dyestuff

a) a pyrazolone having the general formula I



(1)

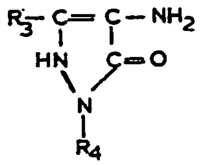
wherein R represents a hydrogen atom, an alkyl residue having from 1 to 6 carbon atoms or a phenyl residue, and

X represents a NH_2, NHR_1, NR_1R_2 group, wherein R_1 and R_2 are alkyl residues having from 1 to 4 carbon atoms or X is the OH group, and

b) an aromatic, di- or polyfunctional amine having at least one primary amino group and a further functional group as hereinafter defined in the para position, or

a 4-aminopyrazolone.

Preferably used are 4-aminopyrazolones of the general formula



wherein R_3 and R_4 each represent a hydrogen atom or an organic residue having from 1 to 10 carbon atoms.

The organic residue R_3 of the 4-aminopyrazolone represents, for example, an alkyl residue with from 1 to 10 carbon atoms, or an aryl or heterocyclic residue. Further, functional groups may be present in R_3 such as —OH, —NH_2, —$NHCH_3$, —$N(CH_3)_2$ or halogen atoms, particularly chlorine. The following groups are also suitable as said organic residues: —COOH, —COOR′, —CONHR′, —CONR′R″, wherein R′ and R″ indicate an alkyl or hydroxyalkyl residue having from 1 to 4 carbon atoms.

The organic residue R_4 of the 4-aminopyrazolone consists of an alkyl residue with from 1 to 10 carbon atoms or of an aryl or heterocyclic residue. Further, functional groups may be present in R_4. Particularly suitable are hydrocarbon residue with from 1 to 10 carbon atoms containing —OH, —NH_2, —COOH, —$CONH_2$, —SO_3H and —SO_2NH_2 as functional groups.

A particularly suitable aromatic residue is a phenyl residue which may contain alkyl or hydroxyalkyl groups with from 1 to 4 carbon atoms or other substituents such as NH_2, OH, COOH, $CONH_2$, SO_3H and SO_2NH_2.

It is frequently an advantage to use 4-aminopyrazolones in the form of their salts, preferably hydrochloride, because this reduces their sensitivity to air.

A suitable aromatic di- and polyfunctional amine, is for example, p-phenylenediamine, p-toluylenediamine, p-aminodimethylaniline, p-aminophenol, p-diaminoanisol, or compounds of the kind mentioned which further have

[*Price 5s. 0d. (25p)*]

one or several functional groups which are OH—, NH_2—, NHR_1 or NR_1R_2 wherein R_1 and R_2 are an alkyl or hydroxyalkyl residue having from 1 to 4 carbon atoms groups. The aromatic di- or polyfunctional amine or the 4-aminopyrazolone is preferably used in approximately molar quantities in relation to the pyrazolones substituted in the 3 position. Generally, it is no advantage if the pyrazolones substituted in the 3 position are present in excess or in deficient quantity. Mixtures of the individual dyestuff components can also be used.

The dye can be developed, as is the case with other oxidation dyes, either by atmospheric oxygen or by chemical oxidants, preferably hydrogen peroxide or its addition products particularly those with urea, melamine and sodium borate. The hair is dyed at temperatures of from 15° to 40°C. preferably at room temperature.

The dyes can be applied in the form of aqueous solutions, but particularly in the form of a cream or emulsion. For this purpose, the dyestuff components can be mixed with any desired surface active substances, particularly anionic or non-ionogenic. Suitable surface active substances are, in particular, alkylbenzole sulphates, fatty alcohol sulphates, alkyl sulphonates, fatty acid ethanol amides, addition products of ethylene oxide with fatty alcohols and alkylphenols.

Absorptive power of the above dyestuffs is good even when they are mixed with the substances listed. The hair dyes can therefore be produced in the form of shampoos, particularly cream shampoos, which are frequently desirable in practice.

Thickening agents can be admixed to the hair dyes according to the invention, such as methyl cellulose, starch, higher fatty alcohols, vaselines, paraffin oil and fatty acids or perfume oil or hair conditioning agents such as pantothenic acid and cholesterine.

The additives are used in the quantities customary for the purpose. Suitable wetting agent additions are quantities of 0.5—30% and, of thickening agents, quantities of 0.1—25%, in relation to total composition in both cases. The concentration of dyestuff is up to 5% depending on application, preferably 0.1—2%, again in relation to total composition.

The hair dyes can be applied in a weakly acidi, neutral, or, in particular, alkaline pH range. The results obtained with the above hair dyes have good light-resistance, washing, and friction properties and can easily be removed, by contrast with conventional dyestuffs based on oxidation dyes, by using reduction agents such as sodium hydroxymethane sulphinate.

EXAMPLE 1:

2.835 parts by weight (0.01 mol) of the hydrochloride of 1 - phenyl - 4 - amino-pyrazolone - 3 - carboxylic acid ethyl ester and 0.99 parts by weight (0.01 mol) 3 - amino-pyrazolone are dissolved in an emulsion of 10 parts by weight fatty alcohols C_{16}—C_{18}, 10 parts by weight fatty alcohol sulphate (industrial mixture C_{16}—C_{18}) and 75 parts by weight water, and the pH is adjusted at 9.5 by addition of ammonia. Make up with water to 100 parts by weight. The colour cream obtained will dye naturally grey hair orange-brown within 20 minutes after mixing with 33 parts by weight 30% hydrogen peroxide.

EXAMPLE 2:

With the same procedure as in Example 1, but using the compounds listed in Table 1 below as components a) and b) and adjusting the pH given in each case with ammonia and acetic acid, grey human hair was dyed with the results stated in the right-hand column of the table.

The dyestuff components were used in molar quantities. The total quantity of components are a), and b), in the emulsion was 3 g in each case, the duration of action was 25 minutes at room temperature.

TABLE

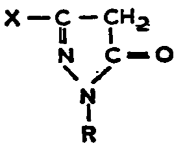
Dyestuff components

No.	a)	b)	pH	Colour
1	3-amino-pyrazolone	4-aminopyrazolone-3-carboxylic acid-ethyl-ester, hydrochloride	9	Orange-brown
2	1-phenyl-3-amino-pyrazolone	1-phenyl-4-aminopyrazolone-3-carboxylic acid amide, hydrochloride	7	Orange-brown
3	3-amino-pyrazolone	1-phenyl-4-amino-pyrazolone-3-carboxylic acid-β-hydroxy-ethyl-amide, hydrochloride	9.5	Orange-brown
4	3-amino-pyrazolone	p-toluylenediamine	9.5	Warm brown
5	1-phenyl-3-amino pyrazolone	p-aminophenol	9.5	Doe brown (reddish brown)
6	3-amino-pyrazolone	p-dimethylamino-aniline	10	Red-violet
7	1-phenyl-3-amino-pyrazolone	p-dimethylamino-aniline	7	Red-violet
8	1-phenyl-3-amino-pyrazolone	p-dimethylaminoaniline	9.5	Red-violet
9	1-phenyl-3-hydroxy-pyrazolone	1-phenyl-4-amino-pyrazolone-3-carboxylic acid amide, hydrochloride	7.5	Yellow
10	1-phenyl-3-hydroxy-pyrazolone	1-phenyl-4-amino-pyrazolone-3-carboxylic acid amide, hydrochloride	9.5	Yellow
11	1-phenyl-3-amino-pyrazolone	p-diaminoanisol	9.5	Brown-violet

WHAT WE CLAIM IS:—

1. A composition for dyeing human hair comprising a dyestuff containing

a) a pyrazolone having the general formula



(1)

I

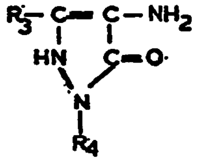
wherein R represents a hydrogen atom, an alkyl residue having from 1 to 6 carbon atoms or phenyl residue, and

X represents an NH_2—, NHR_1, NR_2R_2—group wherein R_1 and R_2 are alkyl residues having from 1 to 4 carbon atoms or X is the OH group and

b) an aromatic di- or polyfunctional amine with at least one primary amino group and a further functional group as hereinbefore defined in the para position or

a 4-aminopyrazolone.

2. A composition as claimed in claim 1 wherein the 4-aminopyrazolone is one of the general formula



wherein R_3 and R_4 represent a hydrogen atom or an organic residue having from 1 to 10 carbon atoms.

3. A composition as claimed in claim 1 or 2 in which the pyrazolone component of formula I and the amine and/or 4-aminopyrazolone components are present in substantially equimolar amounts.

4. A composition as claimed in claims 1 to 3 in which the dyestuff is present in an amount up to 5% relative to the total composition.

5. A composition as claimed in claim 4 in which the dyestuff is present in an amount of from 0.1 to 2% relative to the total composition.

6. A composition as claimed in claims 1 to 5 which further contains a wetting agent and/or thickening agent.

7. A composition as claimed in claim 6 which the wetting agent is present in an amount of from 0.5 to 30% and the thickening agent in an amount of from 0.1 to 25%, relative to the total amount of composition.

8. A composition substantially as hereinbefore described with reference to any of the foregoing Examples.

9. A process of dyeing hair comprising applying a composition as claimed in any of claims 1 to 8 to the hair optionally in conjunction with a developer solution.

10. A process as claimed in claim 9 which is effected at a temperature of from 15° to 40°C.

11. A process as claimed in claim 9 or 10 wherein the developer solution is a solution of hydrogen peroxide or its addition products with urea, melamine or sodium borate.

12. A process as claimed in any of claims 9 to 11 which are effected within the alkaline pH range.

13. A process of dyeing hair, substantially as hereinbefore particularly described with reference to any of the foregoing Examples.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1.
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.